

## HYDROGEN SULFIDE OXIDATION BY NAPHTHOQUINONE COMPLEXES THE HIPERION PROCESS

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**ABSTRACT:** Removal of hydrogen sulfide from gas streams has historically been achieved using a variety of oxidizing agents, including various quinone/metal combinations and iron chelates. Because of its high redox potential, naphthoquinone can be the basis of a highly efficient catalyst system which lends itself to commercial application in an uncomplicated equipment configuration. Both the Hiperion process and its predecessor, the Takahax process (used widely in Japan), make use of naphthoquinone complexes to effectively oxidize hydrogen sulfide to elemental sulfur. The basic chemistry of the process involves oxidation of hydrogen sulfide by a catalyst containing a naphthoquinone/metal complex and re-oxidation of the catalyst by air. This chemistry takes place either in a single absorber/oxidizer column when air is present in the gas or in separate absorber and oxidizer columns for sour gas. Commercial Hiperion units are currently treating refinery gas streams and digester biogas at three locations in the United States. In addition, the process has been demonstrated in pilot plant operation on coal-derived synthesis gas as well as various sour air streams.

### Historical Development

During the late 1800's, producers of town gas in England became concerned with the detrimental effects which hydrogen sulfide had on equipment in which their gas was burned. An early attempt at removing the hydrogen sulfide involved passing the gas through beds containing hydrated ferric oxide supported on a media such as wood chips (known as iron sponge). The ferric oxide reacted with the  $H_2S$  to form ferric sulfide. These beds could in turn be purged with air to oxidize the ferric sulfide to elemental sulfur and ferric oxide, which could be used to react with additional  $H_2S$ . Although this method was relatively effective in removing hydrogen sulfide, it required large plot areas and was very labor intensive. When the bed became completely spent, it was necessary to manually remove and dispose of the iron sponge. This process was made especially difficult by the pyrophoric nature of the spent material.

The next step in the evolution of  $H_2S$  removal processes involved a variety of liquid contacting processes. Some of these involved chemistry similar to that employed in the iron sponges, i.e., suspension of iron oxide in an alkaline solution such that reactions similar to those in the iron sponge could occur. Others involved scrubbing with solutions containing various oxygen carriers such as thioarsenates, polythionates, iron-cyanide compounds, and various organic compounds. Many of these found some commercial application but others were either too specialized in application or not commercially viable.

The current generation of hydrogen sulfide removal processes began when it was discovered in the 1920's that certain organic compounds used in the dye industry were effective in oxidizing hydrogen sulfide to elemental sulfur. Several processes using various materials derived from the dye industry were developed in the following decades. These processes, known as liquid redox processes, employed successive cycles of oxidation of hydrogen sulfide by a catalyst containing an oxidizing agent followed by re-oxidation of the catalyst with air.

Work conducted in the 1950's by the Clayton Aniline Company, Ltd. in conjunction with the Northwestern Gas Board of England resulted in the discovery that various quinone compounds were effective oxidants for  $H_2S$ . These compounds, shown in Figure 1, which included derivatives of benzoquinone, duroquinone, naphthoquinone, and anthraquinone, had the ability to react with hydrogen sulfide to form the respective hydroquinone along with elemental sulfur. The hydroquinone could in turn be oxidized with air back to the quinone form. This work resulted in the development of the original Stretford process which used anthraquinone di-sulfonic acid (ADA) and which was subsequently applied in several commercial applications. However, the kinetics of the ADA/ $H_2S$  reaction were sufficiently slow that large circulation rates and liquid inventories were required. The process was subsequently enhanced by the addition of vanadium salts which significantly increased the kinetics of the reaction and permitted a reduction in circulation rates and liquid inventories. In the modified process, hydrogen sulfide was oxidized by vanadium and the ADA served as a catalyst for the re-oxidation of the vanadium.

Concurrent with the research on ADA and the development of the Stretford process in England, work on other quinone compounds was being conducted in Japan under the sponsorship of Tokyo University and the Tokyo Gas Council. The objective of this research was to develop a hydrogen sulfide oxidation process which would avoid the problems of existing processes (such as side reactions which required a liquid purge and the use of heavy metals), be more efficient, and be tailored to the needs of Japanese industry. The results of this research were used to develop the Takahax process, which uses 1,4 naphthoquinone-2-sulfonic acid as the active agent in the catalyst. This compound has a redox potential which is more than double that of anthraquinone di-sulfonic acid, (refer to Table 1) and thus promotes rapid conversion of  $H_2S$  to sulfur without the addition of vanadium or other toxic chemicals. The Takahax process is currently in use at over 200 installations in Japan, with applications ranging from coke oven gas to municipal digester gas.

Following the commercialization of the Takahax process, work with naphthoquinone was continued, and improved methods for synthesis of both 1,4 Naphthoquinone and 1,4 Naphthoquinone-2-sulfonic acid were developed. Further research resulted in the development of a naphthoquinone/metal complex or chelate which permits an increased rate of re-oxidation of the catalyst after reaction with  $H_2S$  and therefore results in a significant reduction in reaction residence time requirements as compared to Takahax or other liquid redox processes. This improved process, which is known as the Hiperion process, has been commercialized in the United States and is now in commercial operation at three locations. This paper will discuss the chemistry and flow scheme of the Hiperion process and will review operating results covering a wide range of  $H_2S$  removal applications in both the commercial and pilot plant operations.

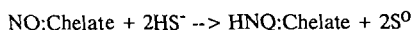
#### Hiperion Chemistry

The basic reactions for liquid phase oxidation of hydrogen sulfide, with the subsequent reoxidation of the catalyst is similar for all liquid redox processes. The hydrogen sulfide is first dissolved in an alkaline solution where it dissociates to a bisulfide ion and a proton:

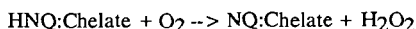


This reaction is, of course, pH dependent. At pH below 7, the undissociated  $H_2S$  is the predominant species, and above pH=9 the  $S^{2-}$  ion predominates. Since the oxidants used in these processes react with the  $HS^-$  ion, it is critical that pH be maintained in the range of 8-9.

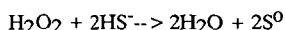
In the Hiperion process, the HS<sup>-</sup> ion is oxidized by the naphthoquinone chelate to elemental sulfur and the quinone is reduced to the hydroquinone form:



The hydroquinone chelate is subsequently reacted with oxygen in atmospheric air to form the quinone chelate and hydrogen peroxide:



Since hydrogen peroxide is an extremely active oxidation agent, it quickly reacts with any residual HS<sup>-</sup> to form sulfur and water:



As discussed later in the description of the Hiperion process flow scheme, the oxidized quinone chelate is returned to the absorber column to further react with hydrogen sulfide.

This description of Hiperion chemistry is obviously very rudimentary and does not address the questions of reaction mechanism or the exact nature of the naphthoquinone complex which participates in the redox transfer and results in the reduction of hydrogen sulfide to elemental sulfur. Although a great deal of research has been done into the chemistry of various liquid redox processes, a great deal remains to be learned. The research which has led to the development of the Hiperion process is largely empirical rather than fundamental, and the thrust of this paper is to describe the results of commercial and pilot plant operations using the Hiperion system. Examination of the fundamental chemistry of the process will be left for future papers.

#### Mass Transfer Packing

Since the reactions involved in the Hiperion process occur virtually instantaneously, the reaction of hydrogen sulfide with the naphthoquinone chelate is limited by mass transfer considerations. Thus effective mass transfer equipment is critical to effective operation of the process. An additional factor in the development of the process was the inherent tendency of solid elemental sulfur to adhere to any available surface. Thus the development of the Hiperion process also involved the development of a packing medium which would provide effective mass transfer and inhibit plugging. The packing consists of finned hollow balls which rotate and become partially fluidized as gas and liquid pass countercurrently through the beds. This mode of operation provides for effective mass transfer as well as inhibiting the settling of sulfur which would result in plugging in the beds. These "windy balls" have been tested in various pilot plant operations and are currently in use in the commercial Hiperion units.

#### Process Description

The flow scheme of the Hiperion process, which is similar to that of other liquid redox processes and is illustrated in Figure 2, includes two main reaction vessels-- an absorber in which the hydrogen sulfide in the gas is reduced to sulfur by contact with the catalyst and an oxidizer in which the catalyst is regenerated. Equipment is also provided for separation of the solid sulfur from the catalyst.

Sour gas enters the bottom of the absorber column and flows upward through a series of beds of "windy balls" where it is contacted by downflowing catalyst, and the  $H_2S$  is oxidized to solid elemental sulfur which is carried off with the liquid catalyst. The sweet gas then passes out of the absorber and to downstream use as dictated by the specific application. The spent catalyst from the absorber flows into a settling vessel where a portion of the suspended sulfur is settled out and the liquid overflow is pumped to the top of the oxidizer column. In the oxidizer, the catalyst is contacted over beds of windy balls with air which is introduced by a blower at the bottom of the column. The spent catalyst is thereby regenerated to the naphthoquinone chelate form, and residual  $H_2S$  dissolved in the catalyst is oxidized to sulfur by hydrogen peroxide which is formed in the oxidation reaction. Vent gas from the oxidizer can be discharged to atmosphere or used as combustion air in a furnace or other device.

Periodically, the sulfur which has settled to the bottom of the settler vessel is withdrawn and pumped through a plate and frame filter press where the sulfur is removed and the filtrate is returned to the process. The filter cake from the process is 95-98% sulfur. It contains no heavy metals or hazardous constituents and is suitable for disposal in a Class II landfill or for further purification and sale.

After filtration, the filter cake is water washed and air blown to minimize catalyst losses. The wash water is returned to the system where it serves as a primary source of makeup water to replace that lost by evaporation. Catalyst lost with the filter cake is replaced by addition of a small amount of catalyst concentrate after each filtration cycle. The only other chemical makeup requirements consist of a small amount of alkaline solution for pH control.

As with other liquid redox processes, the Hiperion process operates at ambient temperature and is capable of operating at the full range of normal industrial operating pressures.

### Commercial Application

The two naphthoquinone based liquid redox processes, Takahax and Hiperion, have been applied commercially to a wide variety of hydrogen sulfide removal applications, both in Japan and in the United States. As shown in Table 2, Takahax plants are currently being used in Japan for hydrogen sulfide removal from coke oven gas, coal derived gas, town gas, and digester gas. These plants treat gas streams ranging from 2 MMSCFD to over 200 MMSCFD and containing from 700 ppm to 10% hydrogen sulfide. In the United States, the Hiperion process has been commercially applied in oil refinery and municipal digester gas services. In addition, the Hiperion process has been demonstrated on a pilot scale in treating coal derived gas, geothermal gas, offgas from rayon manufacture, and air contaminated with  $H_2S$  (see Table 3).

Hydrogen sulfide removal has become an increasingly important consideration to petroleum refiners as environmental restrictions are tightened and as economic and supply considerations dictate a shift to higher sulfur feedstocks. In order to provide the required hydrogen sulfide removal capability, two refiners in California have installed Hiperion units to treat sour gas streams resulting from processing high sulfur crudes.

The first commercial application of the Hiperion process in the United States was in an asphalt refinery where it is part of an indirect method for removing hydrogen sulfide from heavy gas oil (see Figure 3). Heavy gas oil from vacuum distillation is stripped of hydrogen sulfide in a trayed column by a recirculating stream of nitrogen. The  $H_2S$  laden nitrogen stream is then fed to the Hiperion absorber column where the  $H_2S$  is converted to sulfur. The treated nitrogen stream is then recirculated back to the vacuum gas oil stripper for further sulfur removal. The unit was designed for a nitrogen flow rate of 200 scfm at 20 psig with an  $H_2S$  concentration of 4,000 ppm. However, after being put into service, the  $H_2S$  concentration

of the nitrogen increased to between 10,000 and 20,000 ppm. With design modifications to accommodate the increased sulfur loading, the unit has been operating for over three years and has removed over 40 tons of sulfur annually.

A Hiperion unit has recently been installed in a second refinery application where the treated stream is a low volume, relatively high  $H_2S$  hydrocarbon vent gas stream originating from the overhead system of a vacuum distillation column (see Figure 4). Because of the low flow rate of the sour gas (less than 50 scfm) and the high design  $H_2S$  concentration (greater than 10%), this unit was designed with a recycle stream of treated gas which mixes with the incoming sour gas. This approach reduces the concentration of  $H_2S$  entering the absorber column and thereby improves removal efficiency and reduces the tendency of sulfur to deposit in the absorber. The treated gas from this unit, which contains less than 100 ppm of  $H_2S$ , is used as fuel gas in a refinery furnace.

Hydrogen sulfide removal is also a critical issue in municipal wastewater treatment plants where environmental regulations dictate removal of  $H_2S$  from anaerobic digester gas prior to flaring or use in gas engines. As part of a major modernization program, a municipal treatment plant in the southwestern U.S. has recently installed a digester gas treatment and recovery system which includes a Hiperion unit and which will permit compliance with environmental restrictions as well as providing improved energy recovery. A schematic diagram of this application is shown in Figure 5.

In the treatment plant, digester gas, which is composed of approximately equal amounts of carbon dioxide and methane, is generated at a rate of between 100 and 450 scfm and contains between 1,000 and 2,500 ppm of  $H_2S$ . Because of the variability of the flow rate, the gas is stored in a constant pressure vessel upstream of the Hiperion unit and a portion of the treated gas from the Hiperion absorber is recycled back to the same constant pressure vessel. A low pressure gas blower is used to provide the small amount of pressure required to overcome pressure loss in the gas system. Gas equal in volume to the net gas input is withdrawn from the treated gas stream and compressed for use in gas engines within the plant. This unit reduces hydrogen sulfide in the gas to less than 100 ppm (generally less than 20 ppm) and produces between one and two tons of sulfur filter cake per month. The filter cake from this plant is disposed in the same landfill which receives sludge from the treatment plant.

#### Pilot Plant Experience

In addition to those industries described previously where the Hiperion process has been applied commercially, many other industries have similar hydrogen sulfide removal requirements which can be met by the process. Pilot plant work demonstrations of the process have been successfully conducted in a number of these industries.

Steam from geothermal sources provides a major resource for power generation, but in order to utilize this resource, effective means must be provided to remove the hydrogen sulfide associated with geothermal steam. After power has been extracted from the steam, the  $H_2S$  is concentrated in the remaining non-condensable vent gas. Application of the Hiperion system to this service has been demonstrated in field pilot plant tests. Vent gas containing 10%  $H_2S$  was reduced to less than 100 ppm.

Another area where the Hiperion process can meet sulfur removal needs is in contaminated air streams in municipal treatment plants and other industrial applications. Removal of  $H_2S$  from a variety of contaminated air streams has been demonstrated by a single column pilot plant. Since the air required for oxidation of the catalyst is contained in the air being treated, a separate oxidation column is not required. Both oxidation of hydrogen sulfide and oxidation

of the catalyst take place in a single vessel. Pilot plant operations on three separate sour air streams containing from 100 to 5,000 ppm of  $H_2S$  has successfully been demonstrated using the single column pilot plant.

Manufacture of rayon is another industry where removal of hydrogen sulfide from an air stream is required in order to meet environmental requirements. Hydrogen sulfide and carbon disulfide are both released from the acid bath in which the rayon is produced. In response to this need, a single column Hiperion pilot plant was constructed and operated to demonstrate  $H_2S$  removal in this service. Sour air in this application was consistently reduced from an inlet concentration of 1,400 ppm to an outlet concentration of less than 10 ppm.

The Hiperion pilot plant operation which relates most directly to coal gasification was conducted at the Great Plains coal gasification facility in Buleah, North Dakota. The acid gas from the Rectisol system, which is primarily  $CO_2$ , must be treated for  $H_2S$  removal prior to discharge to the atmosphere. Inasmuch as the original treatment system installed at the plant was plagued with operating problems, the plant initiated a pilot plant program to seek a means of improving the operation of the existing  $H_2S$  removal system or converting it to another system. During a two month test program, the Hiperion process successfully demonstrated its ability to remove  $H_2S$  from streams which were otherwise pure  $CO_2$ .  $H_2S$  in the gas was reduced from inlet levels of 1% to outlet levels of less than 100 ppm (Figure 6). In addition, the pilot plant operation successfully demonstrated the effectiveness of the windy ball packing in eliminating plugging of the absorber bed as a major operating problem.

As described above, the various commercial installations and pilot plant operations of the naphthoquinone based Hiperion process (and its predecessor, the Takahax process) have demonstrated the effectiveness of this technology as a tool for removing hydrogen sulfide from gas streams originating from a variety of industrial and municipal sources. The simplicity and effectiveness of the process make it an excellent candidate in any application requiring removal of hydrogen sulfide from a gas stream.

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TABLE 1  
TYPICAL QUINONE REDOX POTENTIALS  
(E<sup>0</sup> at 25°C)

o Benzoquinone	0.787
p Benzoquinone	0.699
3,4 Phenanthrequinone-1-sulfonic acid	0.677
1,2 Naphthoquinone-4-sulfonic acid	0.625
1,4 Naphthoquinone-2-sulfonic acid	0.535
9,10 Anthroquinone-2-sulfonic acid (ADA)	0.187

TABLE 2  
TAKAHAX APPLICATIONS

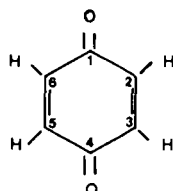
<u>Service</u>	<u>Capacity Range</u> <u>MCFD</u>	<u>H<sub>2</sub>S Content</u>
Town Gas	1.5 - 11.5	700 - 10,500 ppm
Coke Oven Gas	1.9 - 239	2,100 - 3,500 ppm
Digester Gas	1.0 - 14.4	1.7% - 2.8%
Chemical Waste Gas	0.1 - 9.6	0.5% - 10%
Flue Gas	62.2	1,400 ppm
Manufactured Gas	7.7	7,000 ppm

TABLE 3  
HIPERION PILOT PLANT APPLICATIONS

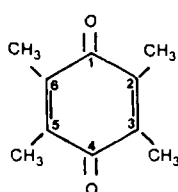
<u>Industry</u>	<u>Service</u>	<u>H<sub>2</sub>S Concentration</u>
Rayon Manufacture	Sour Gas	1,400 ppm
Geo Thermal	Vent Gas	10%
Municipal Treatment Plant	Sour Air	300 ppm
Sulfur Manufacturer	Sour Air	700 ppm
Coal Gasification	Acid Gas	1%

FIGURE 1  
QUINONES USED IN  
HISTORICAL LIQUID REDOX STUDIES

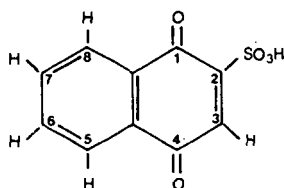
Benzoquinone



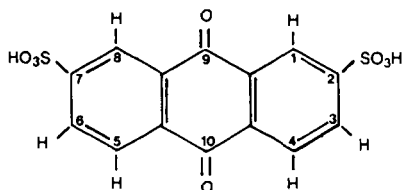
Duroquinone



1,4 Naphthaquinone-2-sulfonic acid



2,7-Anthraquinone-di-sulfonic acid



Source: Reference 2

FIGURE 2  
HIPERION PROCESS

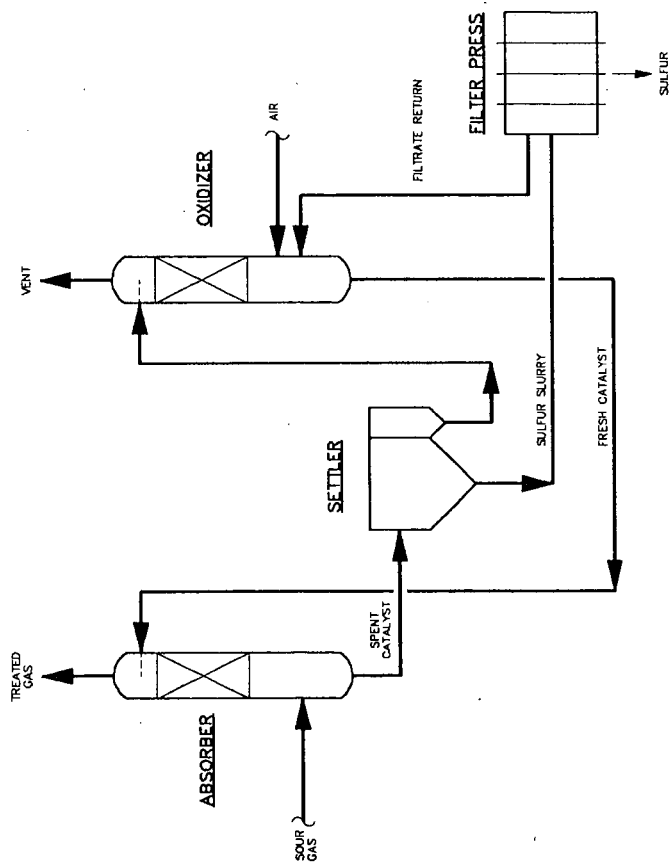


FIGURE 3  
HIPERION PROCESS  
OIL REFINERY APPLICATION  
GAS OIL TREATMENT

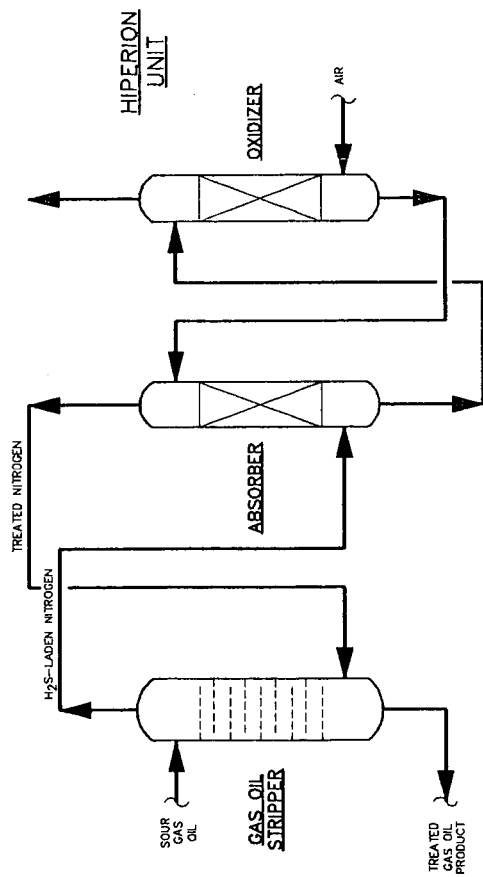


FIGURE 4  
HIPERION PROCESS  
OIL REFINERY APPLICATION  
VENT GAS TREATMENT

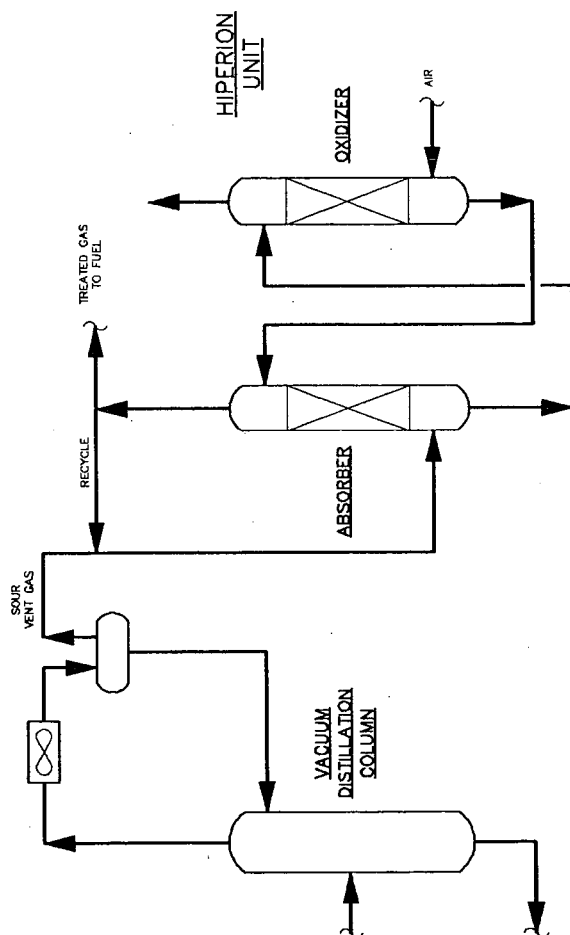


FIGURE 5  
HIPERION PROCESS  
DIGESTER GAS APPLICATION

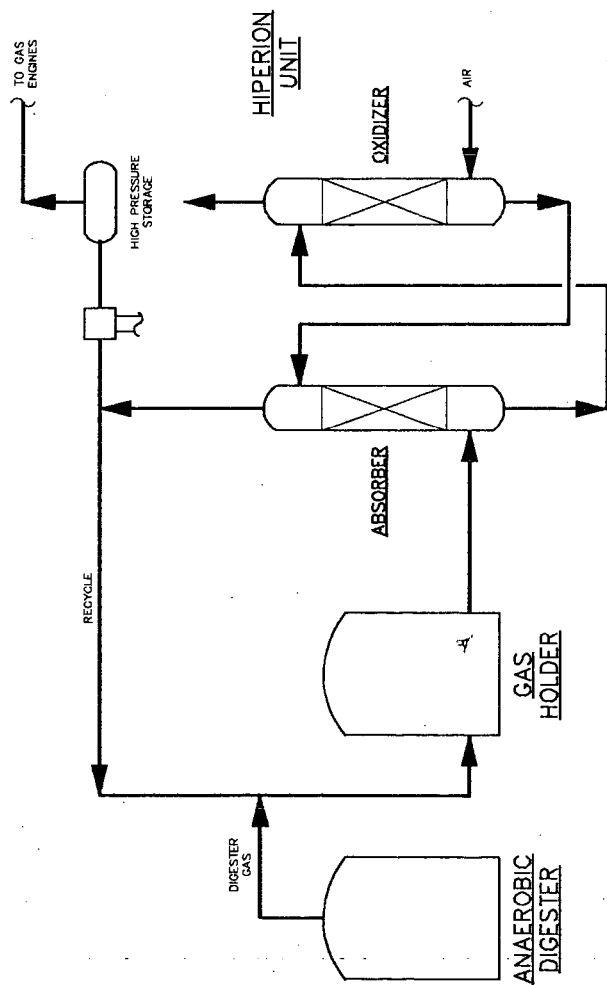


FIGURE 6  
HIPERION PILOT PLANT  
COAL DERIVED GAS

